ON

PHENYLBUTYRO-LACTONE

AND CERTAIN

OXY-ACIDS FROM THE AROMATIC ALDEHYDES.

INAUGURAL DISSERTATION

SUBMITTED TO THE

FACULTY OF MATHEMATICS AND NATURAL SCIENCES OF THE KAISER WILHELM UNIVERSITY, STRASSBURG,

FOR THE

ACQUISITION OF THE DOCTORATE,

BY

HARRY W. JAYNE.
(PHILADELPHIA, Pa.)

WIESBADEN.
L. SCHELLENBERG'SCHE HOF-BUCHDRUCKEREI
1882.

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The following investigation was made in the laboratories of the University of Strassburg under the direction of Prof. FITTIG — to my honored instructor I tender my thanks for the aid and constant attention given me while with him.

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In April 1877 appeared the interesting article by Perkin[1]) on the formation of cinnamic and other acids from the aromatic aldehydes.

Among the many acids obtained during the course of this investigation were two with the empirical formula, $C_{10}H_{10}O_2$.

One of these was obtained by heating benzylic aldehyde, in sealed tubes, with propionic anhydride and sodic propionate. The other, by acting on the same aldehyde with succinic anhydride and sodic succinate.

The first, being prepared from a homologue of acetic acid, he supposed to be constituted like cinnamic acid and having the formula;—

$$C_6H_5 - CH = CH - CH_2 - COOH$$

He gave it the name phenylcrotonic acid, and represented the formation of this and of cinnamic acid by the equations;—

$$C_6H_5 - CHO + CH_3 - COOH^{2}) = C_6H_5 - CH = CH - COOH + H_2O$$

$$C_6H_5 - CHO + CH_3 - CH_2 - COOH^{2}) = C_6H_5 - CH = CH - CH_2 - COOH + H_2O$$

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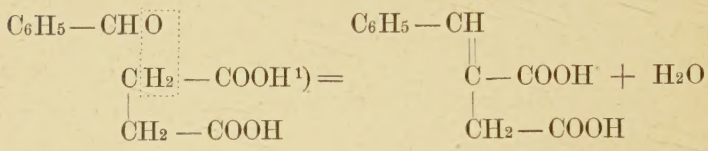
[1]) Perkin, Journal of the Chem. Soc. 1877, **1**, 388.

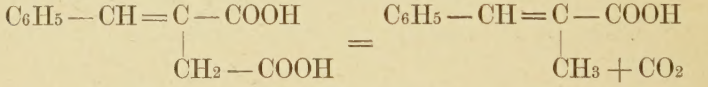
[2]) Written as acid for convenience.

The acid resulting from succinic anhydride and sodic succinate he called *iso*-phenylcrotonic acid, and considered the reaction as taking place in two phases.

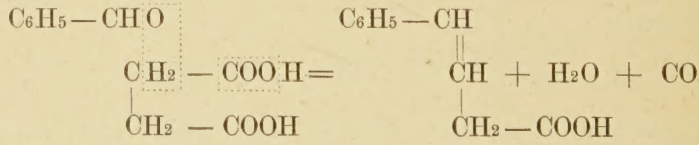
I. The formation of a dibasic acid;—



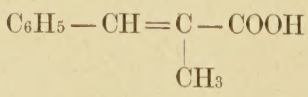
II. The splitting up of this acid into iso-phenylcrotonic acid and carbonic anhydride;—



These suppositions were opposed at the time, Fittig[2]) remarked that he could see no ground for this belief, as it was improbable that carbonic anhydride would split off from *that* carbon atom which took no part whatever in the reaction. According to his views it was much more probable that the reaction was represented by the equation;—



The acid obtained by propionic anhydride should have the formula;—



[1]) Written as acid for convenience.

[2]) Fittig, Annalen **195**, 172.

Later, Conrad[1]) and Hodgkinson in the course of their investigation on the "Synthesis of the phenylated acids of the fat series" obtained an acid from benzylic phenylbutyrate,— C_6H_5 — C_3H_6 — $COOC_7H_7$, by saponification. This acid had the formula $C_{10}H_{10}O_2$ and possessed all the properties of *that* phenylcrotonic acid obtained from propionic anhydride. A full description of it and several salts was given.

Still later Conrad[2]) and Bischoff prepared a quantity of pure phenylcrotonic acid from propionic anhydride and from benzylic phenylbutyrate.

They compared the acids so obtained. Their salts, as also the melting and boiling points of the acids were found to be identical. By reduction of both acids one and the same phenylbutyric acid was obtained. This latter was also prepared in two different ways by synthesis.

I. From methyl-benzylmalonic ether by saponification and heating the acid so formed, whereby one carboxyl group is broken up.

II. By the action of benzylic chloride and sodic ethylate on methyl aceto-acetic ether, a benzyl-methyl-acetoacetic ether being obtained.

The same compound resulted from the action of methylic iodide on the sodium compound of benzyl-acetoacetic ether. From this by saponification is obtained the acid;—

$$C_6H_5 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - COOH$$

This, as already stated, was also prepared by reduction of phenylcrotonic acid with nascent hydrogen, and in consequence the formula of the latter must be;—

$$C_6H_5 - CH = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - COOH$$

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[1]) Conrad and Hodgkinson, Annalen **193**, 316.

[2]) Conrad and Bischoff, Annalen **204**, 188.

The iso-phenylcrotonic acid being comparitively little known, I undertook by the advice of Professor Fittig the study of it and its derivatives.

Preparation of the Acid.

Perkin [1]) recommended, in his second paper on the subject, that equal parts of aldehyde and anhydride should be taken, and, together with a smaller quantity of sodium salt, be heated in sealed tubes at 140°. As such a low temperature is sufficient it is not necessary to employ sealed tubes and the reaction can be carried out in a flask provided with a long tube and heated in an oil or paraffine bath.

A mixture, in the above proportions, of succinic anhydride and pure benzylic aldehyde with finely powdered sodic succinate (dried at 140°), was heated about twenty hours at 145°. — During this time a slow evolution of carbonic anhydride took place.

The contents of the flask, a brown resinous mass, was treated repeatedly with boiling water, and the solution filtered. On cooling it deposited long needle-like crystals of the acid. These were filtered off, and from the mother liquor the remaining acid was removed by treating with ether. By repeated crystallization from hot water a very pure acid is obtained in long thin needles.

It melts constantly at 86° and boils at 302°, with a slight final decomposition. It is sparingly soluble in hot water and nearly insoluble in cold. It dissolves very readily in alcohol and ether. The best solvent appears to be warm carbon bisulphide, from which the acid separates, on cooling, in short prismatic crystals surmounted by a very pointed hemipyramid, but so rounded that a measurement of them was impossible.

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[1]) Perkin, Journ. Chem. Soc. 1877, **2**, 388.

The yield of acid is very small, not above two per cent., and although many experiments were made with a view to a larger yield no better results could be obtained. The greater part of the reaction consists of a sticky resinous mass which by distillation gives a suffocating vapor like that of succinic acid, a voluminous mass of coal remaining. The distillate consists apparently of hydrocarbons but it was impossible to separate them further.

Barium Salt $(C_{10}H_9O_2)_2Ba + 3H_2O$. This salt, prepared by warming the acid with baric carbonate, crystallizes by slow evaporation in fine large crystals. It is easily soluble in water.

0,3877 grms of the salt gave 0,0418 grms loss and 0,1752 grms $BaSO_4$ = 0,103 Ba.

	Required for $(C_{10}H_9O_2)_2Ba\ 3H_2O$.	Found. —
Ba	26,70	26,56
H_2O	10,52	10,78

Calcium Salt $(C_{10}H_9O_2)_2Ca + 3H_2O$. The calcium salt is quite easily soluble in water and gives a gum like mass on evaporation on the water bath, but crystallized by spontaneous evaporation beautiful fan-like aggregations of long needles are obtained.

At 60° the salt loses about two and a half molecules of water, the remaining water cannot be driven out under 100° when the salt becomes brown and decomposes, effervescing on treating with acids. A water determination could not be made.

0,2379 grms gave 0,0777 grms $CaSO_4$ = 0,0228 Ca.

	Calculated for $(C_{10}H_9O_2)_2Ca\ 3H_2O$.	Found. —
Ca	9,61	9,60
H_2O	12,98	—

Monobromophenylbutyric Acid.

By the action of concentrated hydrobromic acid on isophenylcrotonic acid one of two possible compounds could be obtained. The bromine would unite with the second carbon atom from the carboxyl group (β position) or with the third carbon (γ position).

According to numerous observations made by Fittig, during his extended studies on the unsaturated acids, it is more than probable that such acids as have bromine (or chlorine) in the β position by treating with watery solutions of alcaline carbonates give hydrocarbons, carbonic anhydride and hydrobromic acid being split off. The β monobromophenylpropionic acid is a good example of this class;—

$$C_6H_5—CHBr—CH_2—COOH = C_6H_5—CH=CH_2 + CO_2 + H_2O$$

β bromophenylpropionic acid — Styrolene

If the bromine is in the γ position, by the same treatment hydrobromic acid is given off and a class of neutral bodies called lactones are formed.

Numerous bodies of this class are known in the fat series, for instance;—

$$CH_3—CHBr—CH_2—CH_2—COOH = CH_3—CH(—O—CO)—CH_2—CH_2$$

γ bromovalerianic acid — valerolactone [1])

$$CH_3—CH_2—CHBr—CH_2—CH_2—COOH = CH_3—CH_2—CH(—O—CO)—CH_2—CH_2$$

γ bromocaproic acid — caprolactone [2])

[1]) Messerschmid, Annalen **208**, 92.
[2]) Bredt, Annalen **208**, 55.

In order to prepare the monobromophenylbutyric acid, finely powdered iso-phenylcrotonic acid was allowed to stand with about ten times its weight of concentrated hydrobromic acid solution (saturated at 0°).

The acid at first partly dissolved but immediately afterwards was precipitated as a floculent mass.

After allowing the whole to stand for several hours the mother liquor was removed as completely as possible by the pump and the slightly yellow mass of crystals dissolved in carbon bisulphide from which solution the acid crystallized in rounded aggregations of small white crystals. The yield of acid is nearly theoretical, only a trace being left in the acid mother liquor.

A weighed portion was treated with sodium amalgam, the solution acidified and the solution precipitated with argentic nitrate.

0,2275 grms gave 0,1755 grms AgBr.

	Calculated for $C_{10}H_{11}BrO_2$.	Found.
Br	32,96	32,83

The compound was therefore monobromophenylbutyric acid. It melts at 69°, but on heating in an open dish, for a short time between 55° and 60° hydrobromic acid is evolved and finally a thick oil is obtained. The latter is insoluble in sodic carbonate and has an aromatic odor.

Phenylbutyrolactone.

On adding a cold solution of sodic carbonate to the above mentioned acid it is decomposed. The liquid becomes milky and on standing deposits an oil heavier than water. The same product is obtained by boiling the bromine acid with water only. The hot solution on cooling becoming cloudy and deposits the

same oily substance. The solution was saturated with potassic carbonate and the oil removed by shaking with ether.

In the strongly alkaline solution only a small quantity of regenerated iso-phenylcrotonic was found.

The etherial solution was evaporated and the residue boiled for a short time with a solution of baric hydrate.

The oil dissolved entirely. The excess of barium was then precipitated by carbonic anhydride. The filtered solution by evaporation gave a white salt, which was dissolved in water and decomposed by hydrochloric acid.

A white precipitate was obtained which by warming the acid solution melted together to a nearly colorless oil. The latter was removed by ether and the etherial solution dried with calcic chloride. The ether was then evaporated and the residue distilled.

It boiled constant, without decomposition, at 306°, only a few drops going over above and below that temperature.

The distillate by cooling in ice solidified to a mass of fine white crystals which did not melt again at the ordinary temperature.

A combustion gave the following results;—

0,2974 grms substance gave 0,1721 H_2O and 0,8076 grms CO_2.

	Calculated for $C_{10}H_{10}O_2$.	Found.
C	74,07	74,05
H	6,17	6,42

It is therefore the lactone of phenylbutyric acid.

It melts at 37° but when once melted it can only be resolidified by long stirring, or the addition of a small crystal of the same substance. It is easily soluble in ether and alcohol from the latter recrystallizing in long flat needles. It is slightly soluble in hot water from which it separates on cooling as an oil.

From carbon bisulphide by spontaneous evaporation large well formed crystals are easily obtained in the course of a few hours. The crystals so obtained are six sided tables, transparent and very brilliant.

I take the occasion here to express my thanks to Dr. Grünling for his kindness in measuring these and other crystals obtained during the course of this investigation:

"System, Rhombic

$$a : b : c = 0{,}6106 : 1 : 0{,}426.$$

The crystals show the following combinations:

$$P,\ \infty\breve{P}2,\ \infty P\bar{\infty},\ \infty P\breve{\infty},\ {}^1/_2P\breve{\infty},\ 2P\bar{\infty},\ 0P.$$

They are generally tabular according to $\infty P\breve{\infty}$, sometimes however, prismatic according to $\infty\breve{P}2$.

		Measured.	Calculated.
P : P	= (111) : (1$\bar{1}$1) =	38° 31′	—
	(111) : ($\bar{1}$11) =	65° 24′	—
	(111) : (11$\bar{1}$) =	78° 25′	78° 32′
$\infty\breve{P}2 : \infty\breve{P}2$	= (120) : ($\bar{1}$20) =	100° 56′	101° 20′
${}^1/_2P\breve{\infty} : {}^1/_2P\breve{\infty}$	= (012) : (0$\bar{1}$2) =	24° 12′	24° 4′
$0P : 2P\bar{\infty}$	= (001) : (201) =	54° 32′	54° 22′
	(111) : ($\bar{1}$20) =	53° 10′	—

Cleavage, well defined according to 0P. Plane of the optic axes = $\infty P\breve{\infty}$. First mean line axis c, second mean line axis a".

The lactone has a pleasant aromatic odor, especially when warm; it is easily volatilized by steam or by warming at 100° in open dishes.

The substance obtained by heating the dry monobromophenylbutyric acid proved to be the lactone. The latter is also obtained if the acid is allowed to stand in the air, when water is absorbed and lactone is formed.

Phenyloxybutyric Acid.

The Barium Salt $(C_{10}H_{11}O_3)_2Ba$ of this acid is prepared by boiling the lactone with baric hydrate, the excess of barium is precipitated by carbonic anhydride and the filtrate evaporated to dryness. On redissolving, a slight residue of baric carbonate is obtained, this is filtered off and on evaporating again the pure salt remains. It is not possible to crystallize it, a gum like mass, which on cooling becomes brittle and glassy, resulting on evaporation. It is moderately soluble in alcohol.

0,2567 grms gave 0,1215 $BaSO_4$ = 0,0714 Ba.

	Calculated for $(C_{10}H_{11}O_3)_2Ba$.	Found. —
Ba	27,67	27,84

This barium salt, on dissolving in water and cooling with ice, by addition of cold acid gives a precipitate of the free oxy-acid. By shaking with ether and spontaneous evaporation of the latter in a cool place, the acid was obtained as a snow-white crust. This was pressed between filter paper and dried over calcic chloride and analysed.

0,2054 grms of the acid gave 0,1233 grms H_2O and 0,5043 grms CO_2.

	Calculated for $C_{10}H_{12}O_3$.	Found. —
C	66,66	66,47
H	6,66	6,67

The acid melts at 75° but heated for a short time in an open crucible between 65° and 70°, water is given off and the lactone is obtained. It is easily soluble in alcohol, ether and carbon bisulphide, from the latter good crystals are obtained. They appear as transparent flat crystals tapering gradually to a point at both ends and always united in groups. The acid is

quite soluble in water if gently warmed and crystallizes again on cooling, but if heated above 80° lactone is formed, very long boiling is however necessary in order to decompose the acid entirely into lactone.

If small quantities of mineral acids are added to the boiling solution the lactone formation is greatly accelerated. The acid dissolves in cold potassic carbonate solution to form salts, the same can be obtained by allowing the lactone to stand for several days with a saturated solution of potassic carbonate.

Silver Salt ($C_{10}H_{11}O_3Ag$). This salt is obtained as a curdy white precipitate on adding argentic nitrate to a solution of the barium salt. It is quite insoluble in water. — By light it is very slightly decomposed.

(I.) 0,2610 grms gave 0,0938 grms H_2O and 0,4028 grms CO_2.
(II.) 0,1680 grms gave 0,0631 grms Ag.

	Calculated for $C_{10}H_{11}O_3Ag$.	Found. I.	Found. II.
C	41,81	42,09	—
H	3,83	3,99	—
Ag	37,63	—	37,56

Since the completion of this investigation Burcker[1]), has prepared the above mentioned oxy-acid by reduction of benzoylpropionic acid. He states that the acid so obtained melted at 31° and boiled at 235°. It will at once be seen that an acid of that composition could not have so low a boiling point, he states moreover that his acid was always accompanied by an oil, showing that he had a mixture of lactone and oxyacid.

There can be little doubt as to the structure of these compounds, the monobromophenylbutyric acid by treating with sodic carbonate gives up hydrobromic acid, the lactone being obtained. As the bromine is probably in the γ position the formula would be;—

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[1]) Burcker, Bulletin Soc. Chimique **37**, 5.

$$C_6H_5-CHBr-CH_2-CH_2-COOH = C_6H_5-CH(O-CO)-CH_2-CH_2 + HBr.$$

The phenylbutyro-lactone is probably the first of this class known in the aromatic series in which the condensation takes place entirely in the side chain.

Of other bodies resembling the lactones only those are known in which two carbon atoms are in the benzol chain, and in the ortho-position to each other. Such are the phtalides and probably cumarin which by treating with baric hydrate give barium salts of oxy-acids.

Di-Bromophenylbutyric Acid.

On adding bromine to a solution of iso-phenylcrotonic acid it is absorbed with great avidity, the solution becoming very hot and hydrobromic acid is evolved.

The resulting acid is impure containing oily compounds. To obtain a pure acid it is necessary to use a dilute solution of iso-phenylcrotonic acid in carbon bisulphide, bromine dissolved in the same solvent being carefully added to the acid, the whole being cooled by ice. On evaporation of the carbon bisulphide but little hydrobromic acid is evolved and the bromine compound is obtained as a crust of small white crystals, melting at 138°.

A portion was treated with sodium amalgam and the bromine precipitated with argentic nitrate.

0,3218 grms substance gave 0,3738 grms AgBr = 0,159 Br.

	Calculated for $C_{10}H_{10}O_2Br_2$.	Found.
Br	49,68	49,44

By the treatment with sodium amalgam the bromine is entirely removed but the saturated acid is not formed, the entire bromine acid is changed to the lactone.

Phenylbutyric Acid.

By treating the lactone with nascent hydrogen it is impossible to break up the lactone ring, not even traces of the phenylbutyric acid being formed.

By reduction of the unsaturated iso-phenylcrotonic acid with a four per cent. amalgam of sodium the saturated phenylbutyric acid however was obtained.

The addition of hydrogen takes place with difficulty in a cold solution, but if heated and the excess of alkali removed continually by sulphuric acid by employing a large excess (15 to 20 times the theoretical quantity) of sodium amalgam the acid is entirely reduced.

By acidifying, shaking out with ether and repeated crystallization from warm water it was obtained pure.

The acid is moderately soluble in warm water and crystallizes on cooling in long flat leaves. The dried acid has a mother of pearl lustre and resembles benzoic acid very much in outward appearance. — It is soluble in all the ordinary solvents. It melts at 47°,5 and boils at about 290°.

0,2280 grms gave 0,1481 grms H_2O and 0,6067 grms CO_2.

	Calculated for $C_{10}H_{12}O_2$.	Found. —
C	73,17	72,57
H	7,31	7,21

Calcium Salt $(C_{10}H_{11}O_2)_2Ca$. This is very soluble in water and cannot be obtained crystallized.

0,4235 grms gave 0,1618 grms $CaSO_4$.

	Calculated for $(C_{10}H_{11}O_2)_2Ca$.	Found. —
Ca	11,05	11,24

The barium salt is obtained in fine crystals, by spontaneous evaporation as very thin oval leaves closely united in rounded groups.

Both these salts decompose at 100°.

In the mother liquor from the preparation of iso-phenylcrotonic acid (and from which the latter had been entirely removed by means of ether) an abundant white precipitate was obtained by hydrochloric acid. This was filtered off and redissolved in boiling water from which, by cooling, were deposited large ball-like aggregations of long brilliant needles, presenting a very characteristic appearance.

The quantity of acid so obtained is three or four times as much as the iso-phenylcrotonic acid resulting from the same reaction.

By recrystallization the melting point remained constant at 99°. — The acid is more soluble in hot water than the iso-phenylcrotonic acid, but very little soluble in cold water. It is extremely soluble in chloroform, alcohol and ether, but perfectly insoluble in carbon bisulphide and by this means can be purified from traces of iso-phenylcrotonic acid which might be present.

The crystals obtained from water show a combination of a prism, nearly right-angled and according to which they are developed, and of small pyramidal end-planes. Perfect basic cleavage.

The crystals are diaxial. A measurement was found to be impossible on account of the high index of refraction.

The acid thoroughly dried in the desiccator was then heated to 100° until constant weight was obtained.

0,2995	grams	substance	lost	0,0068	grams		2,27	per cent.
0,2236	»	»	»	0,0049	»	=	2,19	» »
0,2622	»	»	»	0,0058	»	=	2,21	» »

The acid thus dried, melted at 109°. It was then redissolved in hot water and gave on cooling the same crystals as before, melting at 99°. — The crystals were again dried at 100° when the same lost took place,

0,2075 grams acid gave 0,0049 loss = 2,32 per cent.

so the loss is from water of crystallization.

A combustion was made of the acid dried at 100°, great difficulty was experienced in burning it completely.

0,2270 grms gave 0,1030 grms H_2O and 0,5355 grms CO_2.

	Calculated for $C_{11}H_{10}O_4$.	Found.
C	64,08	64,33
H	4,85	5,04

An acid with the composition $C_{11}H_{10}O_4$ with 2,2 to 2,3 per cent. loss of water of crystallization would have the formula $4C_{11}H_{10}O_4 + H_2O$ — which requires 2,14 per cent. loss.

The acid (previously dried at 100°) on being heated to 150° commenced to evolve carbonic anhydride, on increasing the temperature the evolution became more violent until the thermometer reached about 300° when it remained constant and a slightly yellow oil distilled over and solidified to a fine mass of crystals in the receiver. Towards the end of the distillation suffocating vapors were given off and a small quantity of coal was left.

The distillate dissolved in greater part in a solution of sodic carbonate, a small quantity of an oily substance remaining, this was removed by ether and the etherial solution evaporated. An aromatic oil was left resembling the lactone. — It was insoluble in baric carbonate but dissolved in baric hydrate on warming. After removing the excess of barium the solution was evaporated to dryness, a glassy mass being obtained. A barium determination was made of the dry salt.

0,2642 grms gave 0,1244 grms $BaSO_4$.

	Required for $(C_{10}H_{11}O_3)_2Ba$.	Found.
Ba	27,67	27,66

The substance was in reality the lactone. The amount was from five to six per cent. of the acid distilled.

The alkaline solution of sodic carbonate gave a white curdy precipitate on adding hydrochloric acid. By dissolving in hot water and crystallizing long needles were obtained. They melted at 86° and were easily soluble in carbon bisulphide. From these and other properties it was shown to be iso-phenylcrotonic acid. With the exception of the lactone and iso-phenylcrotonic acid other products could not be obtained in sufficient quantity for examination, small quantities of a hydrocarbon were present. If we except the lactone nearly the whole quantity of the acid distilled is decomposed to iso-phenylcrotonic acid.

Barium Salt $(C_{11}H_9O_4)_2Ba + 3H_2O$. On allowing the acid to stand in cold water with baric carbonate, it dissolves, and on filtering off the excess of barium and allowing the solution to crystallize brilliant crystals of the barium salt are obtained. They are easily soluble in cold water. On heating at 100° water is driven out.

0,2345 grms gave 0,0204 grms loss and 0,0907 grms $BaSO_4$.

	Calculated for $(C_{11}H_9O_4)_2Ba\ 3H_2O$.	Found.
Ba	22,79	22,74
H_2O	8,98	8,70

Calcium Salt $(C_{11}H_9O_4)_2Ca + 2H_2O$. The calcium salt is obtained by neutralization with calcic carbonate, it is very soluble in water, by slow evaporation over sulphuric acid silky fern-like crystals are obtained. Water is first driven out at 135° one molecule being given off easily, but before the second can be removed the salt decomposes and effervesces with acids.

(I.) 0,2220 grms gave 0,0627 grms $CaSO_4$.
(II.) 0,2551 grms gave 0,0727 grms $CaSO_4$.

	Required for $(C_{11}H_9O_4)_2Ca\ 2H_2O$.	Found. I.	Found. II.
Ca	8,23	8,30	8,38
H_2O	7,40	—	—

This salt, as stated above, decomposes on heating to 140° and at that temperature a nearly constant weight is finally obtained, if the slightly browned contents of the crucible are then treated with water nearly the whole dissolves and on addition of hydrochloric acid to the filtered solution a precipitate is obtained. This is soluble in carbon bisulphide and on evaporation gives white crystals that melt at 86°. It proved to be iso-phenylcrotonic acid.

Silver Salt ($C_{11}H_9O_4Ag$). On adding argentic nitrate to a solution of the calcium or barium salt a floculent white precipitate is produced. This can be filtered off and washed with cold water. The dried salt is a white powder but little affected by light. It was impossible to crystallize it.

(I.) 0,3561 grms gave 0,0935 grms H_2O and 0,5487 grms CO_2.
(II.) 0,1897 grms gave 0,0651 grms Ag.

	Calculated for $C_{11}H_9O_4Ag$.	Found. I.	Found. II.
C	42,17	42,02	—
H	2,87	2,92	—
Ag	34,25	—	34,32

In all the above salts the acid is monobasic, but a second series of salts, in which the acid is dibasic, can be obtained by boiling the acid with the hydrates of barium and calcium.

Barium Salt ($C_{11}H_{10}O_5Ba + 2H_2O$). On boiling the acid with baric hydrate solution the former dissolves. The excess of barium was precipitated by carbonic anhydride and the solution filtered. It was then evaporated to dryness and redissolved in water a small residue of baric carbonate remaining.

The salt so obtained is pure. By evaporation small square tabular crystals were obtained. It is sparingly soluble in hot or cold water but when once dissolved the solution can be evaporated to about half its volume before the salt crystallizes again.

It contains two molecules of water, the second cannot be fully driven out before the salt decomposes, at 170°.

(I.) 0,2060 grms gave 0,1205 grms $BaSO_4$.
(II.) 0,2745 grms gave 0,1598 grms $BaSO_4$.
(III.) 0,2273 grms gave 0,1332 grms $BaSO_4$.

	Calculated for $C_{11}H_{10}O_5Ba\ 2H_2O$.	Found. I.	II.	III.
Ba . . .	34,68	34,44	34,23	34,41
H_2O . .	9,11	—	—	—

Calcium Salt ($C_{11}H_{10}O_5Ca$). By boiling with calcic hydrate this salt is obtained. It is sparingly soluble in water and cannot be crystallized. It contains no water of crystallization.

0,2172 grms gave 0,1122 grms $CaSO_4$.

	Required for $C_{11}H_{10}O_5Ca$.	Found. —
Ca	15,27	15,19

Silver Salt ($C_{11}H_{10}O_5Ag_2$). On adding argentic nitrate to a solution of the calcium or barium salt or to the ammonium salt (formed by gently warming the acid with ammonia) a white flaky precipitate is obtained, which by repeated shaking becomes crystalline.

This salt dried in the desiccator gave by combustion the following results.

(I.) 0,3573 grms gave 0,0748 grms H_2O and 0,394 grms CO_2.
(II.) 0,2092 grms gave 0,1028 grms Ag.

	Calculated for $C_{11}H_{10}O_5Ag_2$.	Found. I.	II.
C . . .	30,13	30,08	—
H . . .	2,28	2,33	—
Ag . . .	49,31	—	49,14

If salts of the first series are treated with baric or calcic hydrates they form dibasic salts of the second series.

The free dibasic acid could not be obtained, for on adding mineral acids to the dibasic salts a white precipitate is obtained which when examined proved to be the original monobasic acid.

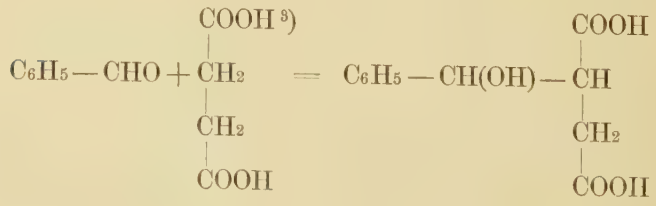
The fact that the acid gives dibasic salts by simply boiling with alkalis, and that on addition of hydrochloric acid the apparently monobasic acid is obtained again, together with the results of the analyses which show that in the monobasic acid and its salts four oxygen atoms are present, give an insight into the character of this acid. The only class of acids that unites these properties in itself is that of the *lactone acids.*

The best known acid of this class is probably the terebic acid, the nature of which has been shown by Bredt[1]) and Geisler[2]).

The terebic acid which contains the lactone ring, besides being a monobasic acid, on treating with alkaline carbonates gives salts with the formula $C_7H_9O_4M$. By boiling with baric hydrate a salt of the diterebic acid, $C_7H_{10}O_5Ba$, is obtained, corresponding to the salts of the second series of this aromatic acid.

If we take account of the formation of this acid in the preparation of iso-phenylcrotonic acid its structure can be easily understood.

By treating benzylic aldehyde with succinic anhydride the following reaction can take place;—



[1]) Bredt, Annalen **200**.
[2]) Geisler, Annalen **208**.
[3]) Expressed as acid for convenience in writing.

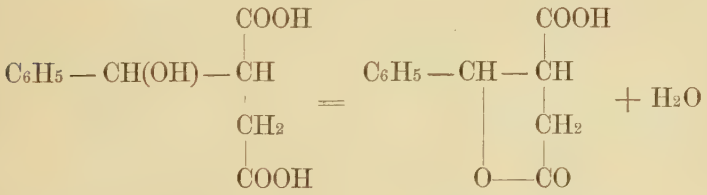
The acid so obtained would be phenyloxysuccinic acid. In this reaction the oxygen in the aldehyde would unite with a hydrogen atom of the succinic acid to form hydroxyl. This is a very common reaction with the aldehydes as is shown by the action of hydrocyanic acid, ammonic hydrate or sodic hydric sulphite;—

$CH_3—CH(OH)—CN$, $C_6H_5—CH(OH)NH_2$, $C_6H_5—CH(OH)SO_3Na$

Still more striking is the condensation by formation of aldol;—

$$CH_3—CHO + CH_3—CHO = CH_3—CH(OH)—CH_2—CHO$$

In the acid obtained by the above reaction two carboxyl groups are present one in the β and the other in the γ position to the hydroxyl group. The acids in the β position are comparitively stable while those with the carboxyl group in the γ position are remarkable for their unstability and with the ease with which they give lactones, when the acid is set free the lactone ring is immediately formed and the other carboxyl group gives the character of a monobasic acid.



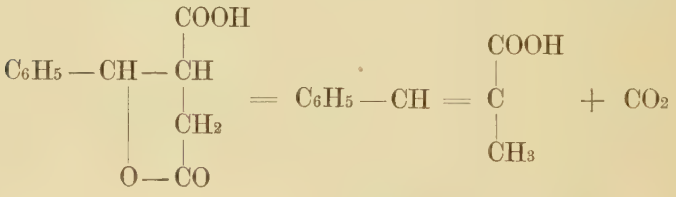
Phenyloxysuccinic Acid. Lactone Acid.

This is very probably the constitution of the acid obtained from the mother liquors from the preparation of iso-phenylcrotonic acid.

It has been seen that during the distillation of this acid carbonic anhydride was evolved and in the distillate several bodies were found.

According to the formula supposed above the decomposition could take place in three different ways.

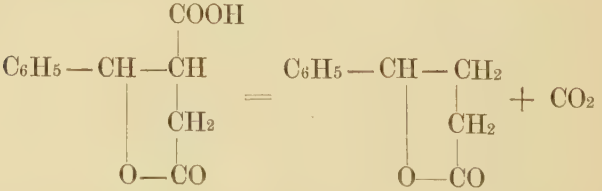
I. The *lactone ring* could split off as carbonic anhydride leaving the carboxyl group intact, a monobasic acid being formed with a molecular change in the molecule. But a glance at the formula would show that this does not take place, as the isomeric phenylcrotonic acid (studied by Conrad and Bischoff) would be formed with displacement of a hydrogen atom from one carbon to the next.



Phenylcrotonic Acid.

In many experiments with the distillation of this acid only the iso-phenylcrotonic acid could be obtained and not even traces of the isomeric acid.

II. The *carboxyl group* could be split off as carbonic anhydride. The simplest case would be that in which the lactone ring is left intact, as;—

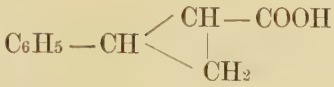


We have seen that this really does occur as lactone is obtained in considerable quantities.

In order to obtain iso-phenylcrotonic acid by the distillation it would be necessary to accept the supposition that a hydrogen atom is moved from one carbon atom to the other.

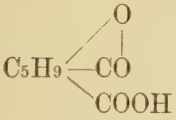
The reaction would possibly take place in the following

manner. From the lactone acid by splitting off carbonic anhydride an acid

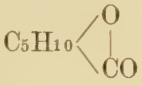


would be formed, and from this the iso-phenylcrotonic would be obtained;—

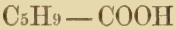
In this case the lactone acid would correspond in almost all its reactions with the terebic acid. The latter by distillation gives off carbonic anhydride, isocaprolactone and the unsaturated pyroterebic acid being formed.



Terebic Acid.



Isocaprolactone.



Pyroterebic Acid.

In this latter case, also, it is necessary to suppose a molecular change as taking place in the formation of the pyroterebic acid.

III. The third possible product would be obtained by the splitting off of two molecules of carbonic anhydride whereby a hydrocarbon would be formed. A hydrocarbon was in reality obtained but not in sufficient quantity to be purified.

By this formula the production of iso-phenylcrotonic acid on heating the calcium salt of the monobasic lactone acid would be explained.

Calcic carbonate would be first formed and from this the carbonic acid would be driven out by the iso-phenylcrotonic acid.

As stated in the introduction to this investigation the condensation was thought to take place between the aldehyde and the anhydride, the sodium salt simply acting as an absorbant for the water formed.

Perkins tried experiments with mixtures of acetic anhydride and sodic propionate as also sodic and plumbic valerate, but cinnamic acid was only obtained.

It has been seen that the iso-phenylcrotonic acid is in the watery solution of the mixture, after the reaction, as a free acid, but that the dibasic acid is present as a sodium salt.

In this case it is without doubt the *sodium* salt which has combined with the aldehyde. The sodium salt formed is probably partly decomposed at the temperature at which the reaction takes place, iso-phenylcrotonic acid being obtained, exactly as is the case with the calcium salt when heated to 140°. The acid is then probably driven out by the more powerful dibasic succinic acid.

In order to see if cinnamic acid is obtained on using acetic anhydride with the salt of a dibasic acid, the following experiments were made.

A mixture of sodic succinate, acetic anhydride and benzylic aldehyde, in the proportion of equal molecules of each, was heated in an oil bath at 125°. The mixture became slightly brown a small quantity of carbonic anhydride being evolved. After heating for about five hours the flask was allowed to cool, and the contents dissolved in water, a tarry residue remained but small in comparison with the residue obtained when succinic anhydride is employed.

The solution was strongly acid and contained the excess of benzylic aldehyde. It was treated with ether and the etherial solution shaken with a solution of sodic carbonate until all the free acid was removed.

The alkaline solution gave with hydrochloric acid an abundant white precipitate. The latter dissolved partly in carbon bisulphide. The residue was well washed with the same solvent and then dissolved in warm water, on cooling needles of the lactone acid were obtained, melting constantly at 99°. In the carbon bisulphide solution iso-phenylcrotonic acid was contained.

The original mother liquor on addition of acids gave also a precipitate which by recrystallization from water was proved to

be the pure lactone acid. *Cinnamic acid* could *not* be found, even in traces, in these solutions. The yield is large; by employing in one operation fifty grammes benzylic aldehyde, with a corresponding quantity of sodic succinate and acetic anhydride and heating to 120° for eight hours, forty grams of pure crystallized lactone acid were obtained.

The whole operation is greatly simplified, doing away with the tedious preparation of succinic anhydride. The mixture is quite fluid and on this account the reaction goes more smoothly. When succinic anhydride is employed the mixture hardens to a cake through which the heat acts but slowly.

By using larger amounts of acetic anhydride the yield is increased. The temperature has also an important influence on the results. If heated on the water bath for fifteen or twenty hours less tar is obtained as also less iso-phenylcrotonic acid but more of the lactone acid is present as free acid.

The amount of liberated acid as also the total yield depending on the length of time the mixture is heated.

If however the mixture is warmed between 125° and 130°, which appears to be the most favorable temperature, the largest yield can be obtained in three or four hours. The acid so obtained contains about twenty per cent. iso-phenylcrotonic acid, which however is easily removed by carbon bisulphide.

Nearly all the acid employed during the course of this investigation was prepared by acetic anhydride.

That the reaction is general is shown by the fact that when sodium salts of the homologues of succinic acid are employed (with acetic anhydride) corresponding dibasic oxy-acids are obtained.

Penfield[1]) heated together sodic pyrotartrate with acetic anhydride and benzylic aldehyde and obtained an acid having the formula $C_{12}H_{12}O_4$, a lactone acid giving two series of salts.

Its constitution and the reaction by which it is formed would probably be represented by the formula;—

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[1]) Penfield, Private Communication, also Berichte XIV, 1824.

$$C_6H_5-CHO+\begin{matrix}COONa\\|\\CH_2\\|\\CH-CH_3\\|\\COONa\end{matrix} = C_6H_5-CH(OH)-\begin{matrix}COONa\\|\\CH\\|\\CH-CH_3\\|\\COONa\end{matrix}$$

The precise rôle played by the anhydrides in these reactions cannot be shown, but without doubt a compound is formed between it and the sodium salts, as on mixing the two heat is evolved and the mixture solidifies to a hard mass.

If the condensation takes place as is shown by the oxy-acid obtained above, then *only* oxy-acids should be obtained by all analogous reactions.

It has been found however that when salts of the monobasic acids are employed only unsaturated acids are obtained. The explanation is very simple. In all these reactions the condensation takes place with the carbon atom of the acid in the α position to the carboxyl group, so that the hydroxyl group would then be in the β position. It is well known with what facility the oxy-acids in the β position give off water and form unsaturated acids, as is the case with hydracrylic and β oxybutyric acids which give acrylic and crotonic acids and also in the aromatic series where phenyllactic acid give cinnamic acid on heating to 180°.

How much easier this splitting off of water would take place in the presence of such bodies as the anhydrides of the fat acids can easily be imagined.

These is one series of acids, however, where the circumstances are somewhat different. These are the acids which have no hydrogen atom on the carbon in the α position. In order to give off water the whole carboxyl group would have to be broken up, and a hydrocarbon formed; as —

$$X-CH(OH)-\begin{matrix}X\\|\\C\\|\\X\end{matrix}-COOH = X-CH=\begin{matrix}X\\|\\C\\|\\X\end{matrix} + CO_2 + H_2O$$

In one experiment, Perkin [1]) employed a mixture of isobutyric anhydride, sodic isobutyrate and benzylic aldehyde and obtained a hydrocarbon $C_{10}H_{12}$ which he called β butenyl-benzene.

In this case there is only one hydrogen atom on the carbon in the α position and this is removed during the reaction.

In order to see if an acid is really formed at first, the following experiments were made.

Phenyloxyisobutyric Acid.

A mixture, in the proportion of equal molecules of each, was made of sodic isobutyrate, isobutyric anhydride and benzylic aldehyde, and the whole heated on the water bath for three or four hours; a small quantity of carbonic acid was evolved and the mixture became very hard.

At the end of this time the contents off the flask was dissolved in water and neutralized with sodic carbonate, and the excess of aldehyde removed by ether. In the etherial solution a small quantity of a hydrocarbon was obtained. It boiled between 183° and 186°, so was the same as that hydrocarbon called β butenyl-benzene.

On acidifying the watery solution an oily acid separated on top, the greater part being isobutyric acid, the whole was boiled for a short time with water whereby the greater part of the isobutyric acid was removed, the remaining solution was shaken out with ether and the ether evaporated; a sticky oily mass was obtained, heavier than water, and from which by dissolving in hot water no crystals could be obtained; on cooling the same oil was always obtained.

In order to crystallize the acid it is necessary to make the barium salt, which is easily soluble in water and crystallizes very finely, and then to decompose this, in a cold solution, by

[1]) Perkin, Journ. Chem Soc. 1879, **1**, 136.

hydrochloric acid, a granular white precipitate is obtained which can be recrystallized from hot water.

The pure acid melts at 134°, is easily soluble in alcohol and ether, nearly insoluble in carbon bisulphide, from a mixture of the last two fine needles are obtained on evaporation.

0,2665 grms gave 0,6669 grms CO_2 and 0,1771 grms H_2O.

	Calculated for $C_{11}H_{14}O_3$.	Found.
C	68,04	68,24
H	7,21	7,38

It is therefore phenyloxyisobutyric acid and its formation would be represented by the formula;—

$$C_6H_5—CHO + \begin{matrix} CH_3 \\ | \\ CH \\ | \\ CH_3 \end{matrix} —COOH = C_6H_5—CH(OH)—\begin{matrix} CH_3 \\ | \\ C \\ | \\ CH_3 \end{matrix} —COOH$$

On heating the acid a few degrees above its melting point it commences to evolve carbonic anhydride and at 150° the evolution becomes quite rapid. By distillation the hydrocarbon β butenyl-benzene is obtained.

The decomposition and the resulting hydrocarbon would therefore be represented by the formula;—

$$C_6H_5—CH(OH)—\begin{matrix} CH_3 \\ | \\ C \\ | \\ CH_3 \end{matrix} —COOH = C_6H_5—CH = \begin{matrix} CH_3 \\ | \\ C \\ | \\ CH_3 \end{matrix} + H_2O + CO_2$$

Phenyloxyisobutyric Acid. β Butenyl-benzene.

The further study of these compounds will be made the subject of future investigation.

CURRICULUM VITAE.

I, Harry Walker Jayne, son of David W. Jayne and Ellen F. Walker, was born in Philadelphia, Penna., U. S. A., June 16th 1857.

From 1864 to 1873 I attended private schools and in the fall of the latter year entered the Scientific Department of the University of Pennsylvania. For five semesters I worked in the chemical laboratories, besides attending lectures on mineralogy, geology, applied chemisty and metallurgy. My instructors were Professors Genth, König, Sadtler and Lesley.

In 1876 I went to Paris, and occupied myself with the study of modern languages.

I removed to Heidelberg in 1877 and entered the chemical laboratories, attending also lectures on chemistry and mineralogy by Professors Bunsen and Rosenbusch.

I returned to Paris in 1878 and from then until the summer of 1880 attended the lectures of Professors Desain, Jamin and Friedel, and working in the physical and mineralogical laboratories of the École des Hautes Études and the chemical laboratory of Professor Wurtz at the École de Medicine.

In 1881 I removed to Strassburg where I spent three semesters under Professors Fittig, Groth and Kundt.